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Vibrational study of hydrated methyl formate complexes in solid neon. Observation for the first time of three isomers for methyl formate-water complex.

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## Abstract

Methyl formate (MF) is an important interstellar medium molecule and it has been the subject of several theoretical and experimental studies in literature. The experimental study of the complexation of this molecule with water has never been undertaken from a vibrational point of view as well as the homodimer (MF)<sub>2</sub>. We highlight for the first time the presence of three isomers for the (MF)<sub>2</sub>, MF-H<sub>2</sub>O and MF-(H<sub>2</sub>O)<sub>2</sub> complexes in solid neon. For the MF-H<sub>2</sub>O complex, we observe without ambiguity three isomers: two where the carbonyl oxygen served as the proton acceptor and one where the alkoxy oxygen was the proton acceptor. For the MF-(H<sub>2</sub>O)<sub>2</sub> complex, we clearly observe three isomers especially by the observation of large frequency shifts of two MF modes. Theoretical calculations at the second-order Møller-Plesset level have been performed to obtain the equilibrium geometries and vibrational spectra at the harmonic level and comparison with experimental data allows us to give structures of observed complexes.

**KEYWORDS:** methyl formate-water complex, Hydrogen Bond, Infrared Spectroscopy, Neon Matrix Isolation, ab initio calculations, isomer.

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## 1. Introduction

Methyl formate (MF) is an important interstellar medium molecule [1,2] and several experimental works try to understand the observed abundance of MF in a variety of astrophysical environments for example in simulating the photodissociation process induced in astrophysical ices [3] or by studying the reaction of MF with hydrogen atoms in a parahydrogen matrix [4]. But few studies have been carried out on its complexation with itself and with water. It therefore seemed important to study these complexations in the solid phase in order to approach the conditions of the interstellar system.

Concerning the MF monomer geometry, two stable structures have been calculated [5,6], a *syn* one, the most stable, and an *anti* one with a difference of relative energy of 5.3 kcal/mol. A recent study at correlated coupled cluster calculations (CCSD(T)-F12) level [7] shows an *anti* - *syn* barrier of  $4616\text{ cm}^{-1}$  (13.2 kcal/mol) with a difference of stability of  $1730\text{ cm}^{-1}$  (4.95 kcal/mol). The fundamental frequencies have been calculated for the both structures and compared with previous gas phase infrared data of MF only for the *syn* observed structure [8-10]. The only vibrational data on the *anti* structure come from two studies in an Ar matrix [11, 12] that show a light-induced isomerization and photochemical transformation of the *syn* form to the *anti* form. Several microwave studies give the rotational transition in the ground [13,14] and first excited torsional states [15] of the *syn* isomer and the rotational characterization of the *anti* has been obtained using several pulsed-jet Fourier transform microwave spectrometers [16]. The homodimer (MF)<sub>2</sub> has been the subject of only two theoretical works [17-18] and in the more complete one [17], 16 low-energy structures were calculated at the second-order Møller-Plesset level (MP2)/ADZ level and the vibrational modes are given for the three more stable structures. No experimental vibrational data exists. For the MF-water complex, ab initio works have been published [18-21], and geometries up to five isomers are given and a set of frequencies is given for the optimized structures. For the MF-(H<sub>2</sub>O)<sub>2</sub> complex, only the optimized geometries are given in reference [18] and there are no experimental data for the MF-H<sub>2</sub>O and MF-(H<sub>2</sub>O)<sub>2</sub> complexes. However two experimental vibrational studies [22,23] exist on the interaction between MF and water ices ~~only~~ in the C=O and C-O stretching regions.

Therefore we have undertaken to study in solid neon the hydration of MF by infrared spectroscopy to obtain vibrational data over a wide spectral range in order to observe the isomers susceptible to exist in solid

phase. So we have recorded the spectra from 80 to 6000  $\text{cm}^{-1}$  of  $(\text{MF})_n\text{-(H}_2\text{O)}_m$  complexes, noted n:m (n and m equal to 1 or 2) isolated in solid neon at 3 K. Harmonic ab initio calculations are also undertaken to support our observations.

After a brief description of the experimental conditions and computational details, theoretical results and experimental spectra will be presented. We will report our calculations performed at the same level, MP2 aug-cc-pVTZ, for all the observed monomers, dimers and 1:1 and 1:2 complexes to make possible comparison between data. An assignment of the different observed bands to isomers of the 1:1 and 1:2 complexes will be proposed with the support of theoretical results.

## 2. Experimental and theoretical details

### 2.1 Experimental apparatus

Samples were prepared by co-condensing MF-Ne and H<sub>2</sub>O-Ne mixtures at a rate of 12 mmol/h onto one of six highly polished, rhodium-plated copper mirrors maintained at 3 K using a closed-cycle helium cryostat (Cryomech PT-405). The temperature was measured using silicon diodes. The MF/Ne molar ratio varies between 100 and 6000, and the neon/water molar ratio varies between 100 and 2000. In the experiments with water it is important to saturate the stainless steel vacuum line to measure accurate pressures in order to avoid the adsorption of the water on the metal walls over time. Absorption spectra were recorded between 80 and 6000  $\text{cm}^{-1}$  on the same sample using a Bruker 120 FTIR spectrometer equipped with suitable combinations of light sources (globar, W filament), beamsplitters (Si/Mylar, KBr/Ge, Si/CaF<sub>2</sub>) and detectors (liquid N<sub>2</sub>-cooled InSb, liquid N<sub>2</sub>-cooled HgCdTe photoconductor, liquid He-cooled Si-B bolometer). All the spectra have been recorded at 3 K and by co-adding 100 scans at 0.1  $\text{cm}^{-1}$  resolution. Natural water and methyl formate (Merck, 99.0 % purity) samples were degassed under vacuum before use. Neon from Air Liquide with a purity of 99.995 % was used.

### 2.2 Computational details

To compare all the vibrational data for the 1:0, 0:1, 0:2, 2:0, 1:1, and 1:2 complexes with each other we have performed calculations at the MP2 level with the Gaussian09 package [24] and the augmented correlation-consistent basis set aug-cc-pVTZ (AVTZ) of Dunning and co-workers [25,26] to obtain

equilibrium geometries, equilibrium ( $D_e$ ) and ground state ( $D_0$ ) binding energies with BSSE and zero point energy (ZPE) corrections, harmonic vibrational frequencies and related infrared intensities.

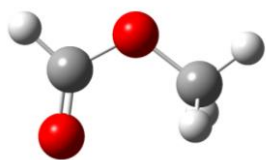
### 3. Theoretical results

For all the complexes and the MF monomer, the most stable calculated geometries and the associated  $D_0$  are reported in Fig.1 and all the frequencies and intensities are given in the supplementary material (Table S1 for  $H_2O$  monomer and dimer, Tables S2 and S3 for MF and  $(MF)_2$ , and Tables S4 and S5 for 1:1 and 1:2 complexes). For the MF monomer the difference of stability between the *syn* and the *anti* structures is about 5 kcal/mol, very high difference. As our aim is to compare theoretical and experimental data and as the *anti* isomer cannot be formed or very little to be detected in the Ne matrix due to its lower energy, so we only consider the *syn* isomer to form the complexes 2:0, 1:1, and 1:2.

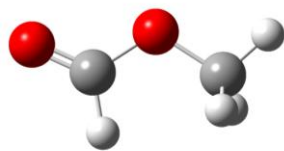
Three  $(MF)_2$  stable structures noted D1, D2, and D3 (Fig. 1) have been calculated and have very close binding energy, 3.9 kcal/mol for D1 and D2, and 3.8 kcal/mol for D3, data comparable to those of reference 17 for both optimized structures. For the 1:1 complex, three stable structures F1, F2, and F3 are calculated with  $D_0$  equal to 4.6, 4.1, and 2.6 kcal/mol, respectively (Fig.1). The structure F1 is formed by a bond between the terminal oxygen of MF and a hydrogen of water and its oxygen pointing to a hydrogen of the  $CH_3$  group. The structure F2 is formed solely by a bond between a hydrogen of  $H_2O$  and the terminal oxygen of MF. The structure F3 is formed by a bond between the central oxygen of MF and a hydrogen of the water molecule. In literature, reference 20 reports the three structures we calculate, reference 18 finds one structure corresponding to F2 and two other ones formed with an *anti* MF monomer and Reference 21 discusses only the F1 structure.

For the 1:2 complex we can remark that G1, G2 and G3 isomers are constructed as the 1:1 isomers F3, F2, and F1, respectively, except that instead of a water molecule it is a water dimer that is bound (Fig. 1). In the only theoretical study [18] on the 1:2 complex one found structure corresponds to the one noted G2 in Fig. 1 and another one is formed with an *anti* MF molecule. Other structures can be considered as those where two water molecules would be separately bound to the MF but with the level of calculations used they are not stable, so not considered.

1:0

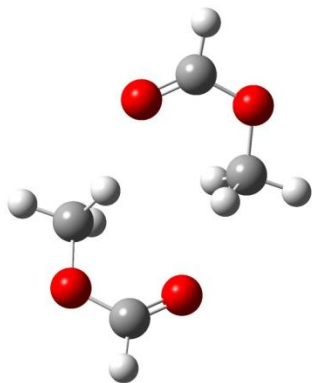


*syn* (Cs)

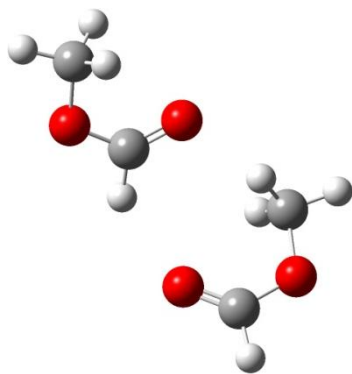


*anti* (Cs)

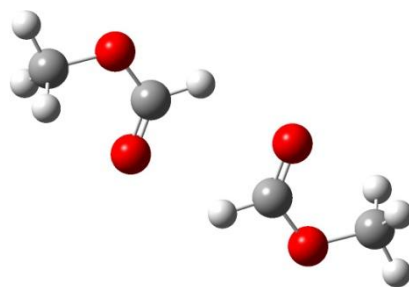
2:0



D1 (C1) 3.9 kcal/mol

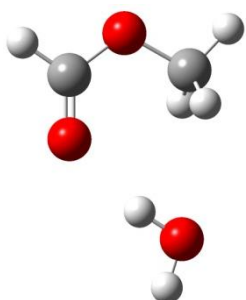


D2 (C1) 3.9 kcal/mol

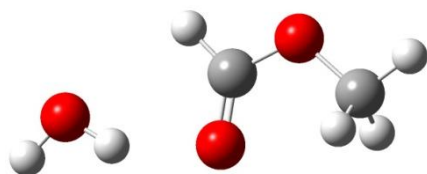


D3(Cs) 3.8 kcal/mol

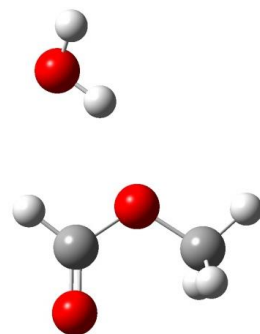
1:1



F1 (CS) 4.6 kcal/mol

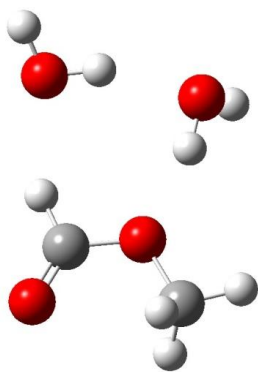


F2 (Cs) 4.1 kcal/mol

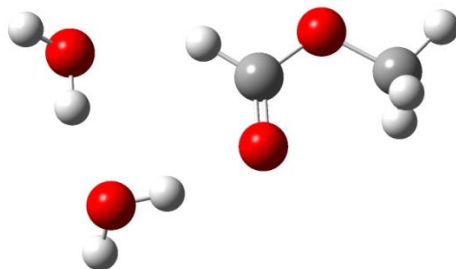


F3 (C1) 2.6 kcal/mol

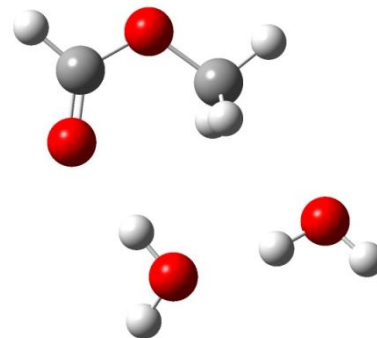
1:2



G1 (C1) 8.6 kcal/mol



G2 (C1) 7.8 kcal/mol



G3 (C1) 6.9 kcal/mol

**Fig. 1.** The most stable calculated structures of different isomers of 1:0 molecule and 2:0, 1:1, and 1:2 complexes. The symmetries of the isomers are indicated in parenthesis.

#### 4. Spectral data and assignments

Our experiments were performed using different concentration ratios of MF/H<sub>2</sub>O/Ne gas mixtures to identify the transitions of the n:m complexes. Figures 2-9 illustrate the IR spectra for different frequencies ranges corresponding to the different modes of MF and water. Table 1 resumes the observed frequencies of MF and (MF)<sub>2</sub> and Tables 2 and 3 frequencies of 1:1 and 1:2 complexes for the MF and H<sub>2</sub>O spectral regions, respectively.

##### 4.1 Monomers and dimers

The infrared absorptions of the H<sub>2</sub>O monomer, dimer, and trimer trapped in solid neon are well known for the fundamental modes, and for many overtones and combinations [27,28].

For MF regions, no band was observed that could be attributed to the MF *anti* isomer, probably it is formed in too small quantities due to its low stability compared to *syn* one. So we consider only the *syn* isomer is present in our matrix, as is the case in argon and parahydrogen matrices [4,11,12] and in microwave and IR gas phase studies [8-15].

The vibrational MF spectrum is well known [8-10] and in Table 1 we report our observed frequencies and assignments of 16 of the 18 modes ( $\nu_{15}$  and  $\nu_{18}$  are not observed). Our data are compared with those obtained in gas phase [8-10] and a deviation of 0.3% on average is measured, so it shows that the neon matrix disturbs the vibration values very little.

We also report in the Table 1 the observed frequencies for the MF dimer, never published to our knowledge. Our results are presented in the Fig. 3a, 4a, 5a, 6b. The MF dimer signatures appear near the MF's fundamentals and were identified through their intensity evolution that must grow with the square of the MF concentration.

**Table 1**MF and (MF)<sub>2</sub> experimental frequencies in solid Ne, and MF in gas phase.

	Assignments <sup>a</sup>	MF		(MF) <sub>2</sub>
		Solid Ne	Gas <sup>b</sup>	Solid Ne
v <sub>12</sub>	δ COC	317.7	325	-
v <sub>17</sub>	τ C-O	340.0		350
v <sub>11</sub>	δ OCO	769.3	767	772. 2, 771.0
v <sub>10</sub>	ν CH <sub>3</sub> -O	927.8	925	917.7
v <sub>16</sub>	γ CH	1032.5	1032	1047.5, 1048.7
v <sub>9</sub>	ρ CH <sub>3</sub>	1166.8	1168	1170.5
v <sub>8</sub>	ν C-O	1211.3	1207	1218.4, 1221.2
v <sub>7</sub>	δ C-H	1375.4	1371	1379.5
v <sub>6</sub>	δ <sub>s</sub> CH <sub>3</sub>	1440.0	1445	1434.9
v <sub>14</sub>	δ <sub>a</sub> CH <sub>3</sub>	1454.1	1454	1458.0
v <sub>5</sub>	δ <sub>a</sub> CH <sub>3</sub>	1466.7	1465	-
v <sub>4</sub>	ν C=O	1752.3	1754	1730.7, 1740.2, 1745.8, 1748.5
v <sub>3</sub>	ν C-H	2945.5	2943	2942
v <sub>2</sub>	ν <sub>s</sub> CH <sub>3</sub>	2978.7	2969	-
v <sub>13</sub>	ν <sub>a</sub> CH <sub>3</sub>	3024.6	3012	3016
v <sub>1</sub>	ν <sub>a</sub> CH <sub>3</sub>	3056.6	3045	3049

<sup>a</sup>MF assignments according to reference 10. <sup>b</sup>Ref 8-10

#### 4.2 (MF)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> complexes

When water and MF are codeposited in neon matrix, a number of new bands appear in the far-infrared region corresponding to the intermolecular modes and near the intramolecular fundamental modes of each monomer in the mid-infrared. All the observed bands for 1:1 and 1:2 complexes are given in Tables 2 and 3 as well as the frequencies of the water monomer and dimer (Table 3). It is important to notice that for some modes we observe several bands that cannot be only the signatures of different trapping sites since the frequency shifts between the bands are too large.



**Table 2**

Observed frequencies ( $\text{cm}^{-1}$ ) and assignment in the far-IR and in MF regions for 1:1 and 1:2 complexes isolated in solid neon.

n:m	Assignment	
1:1	$\nu_{\text{inter}}^{\text{a}}$	104, 110, 248.0, 294.6, 305.4, 471, 482
1:1	$\nu_{17}$	352.0
1:1	$\nu_{11}$	765.2, 771.2, 774.9
1:1	$\nu_{10}$	917.3, 915.5
1:1	$\nu_9$	1174.5
1:2	$\nu_9$	1135.0
1:1	$\nu_8$	1221.5, 1224.0, 1231.2
1:1	$\nu_7$	1380.9
1:1	$\nu_6$	1443.3
1:1	$\nu_5$	1462.0
1:1	$\nu_4$	1729.6, 1731.5, 1736.5, 1737.4, 1758.7
1:2	$\nu_4$	1712.0, 1761.2
1:1	$\nu_3$	2954.9

<sup>a</sup>: Intermolecular modes.

**Table 3**

Observed frequencies ( $\text{cm}^{-1}$ ) and assignment in  $\text{H}_2\text{O}$  regions for 1:1 and 1:2 complexes isolated in solid neon.

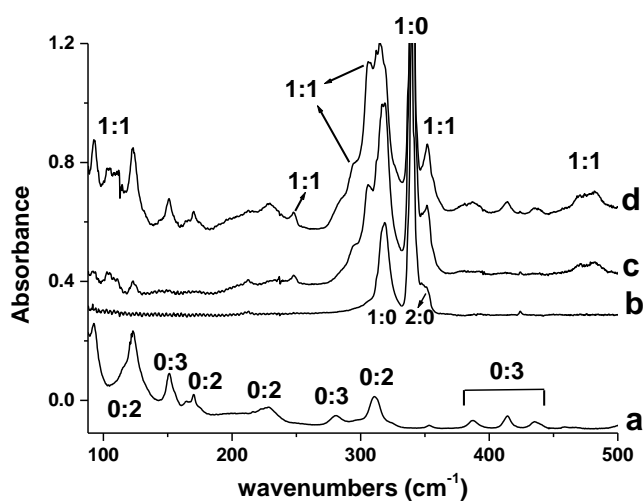
n:m	Assignment	
0:1	$\nu_2$ (nrm <sup>a</sup> )	1595.6
0:2	$\nu_2$	1599.2 PA <sup>b</sup> , 1616.5 PD <sup>b</sup>
1:1	$\nu_2$	1601.9, 1608.1, 1612.6
1:1	$\nu_2 + 305$	1911.4
1:1	$\nu_3$	2954.9
0:2	$2\nu_2$	3163.0, 3193.7
1:1	$2\nu_2$	3176.8, 3179.3
1:2	$\nu_1$	3447.5, 3459.6, 3466.9, 3503.1, 3512.1, 3537.6
1:1	$\nu_1$	3571.7, 3573.4, 3579.4, 3580.8, 3628.8
0:2	$\nu_1$	3590.5 PD, 3660.6 PA
0:1	$\nu_1$ (nrm)	3665.4
1:1	$\nu_3$	3723.4, 3725.8, 3728.5, 3736.9, 3741.5
0:1	$\nu_3$ (nrm)	3761.0
1:1	$\text{H}_2\text{O } \nu_1 + \nu_2$	5166.5, 5178.5, 5213.8
1:2	$\text{H}_2\text{O } \nu_1 + \nu_2$ PD	5124
1:1	$\text{H}_2\text{O } \nu_2 + \nu_3$	5319.3, 5324.9
1:1	$\text{H}_2\text{O } \nu_1 + \nu_3$	7219.9, 7232.1

<sup>a</sup> nrm : no rotating monomer

<sup>b</sup>PD: proton donor and PA: proton acceptor in water dimer

#### 4.2.1 Intermolecular spectral region

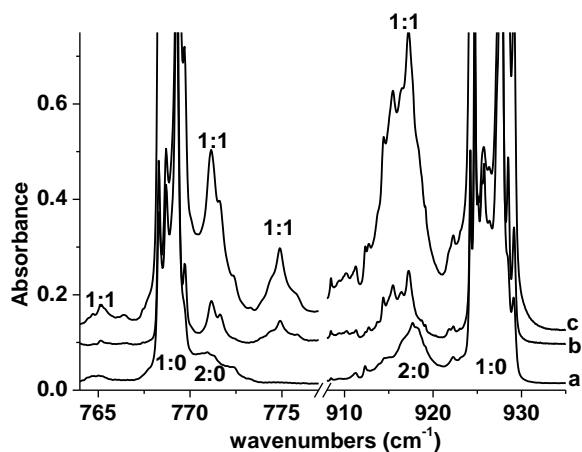
With our experimental set-up we can probe the intermolecular modes from  $80\text{ cm}^{-1}$  but in this region water dimer and trimer have many signatures [27,28] as shown in Fig. 2a. Two very close bands at  $104$  and  $110\text{ cm}^{-1}$  appear when the MF and water molecules are deposited together as well for the bands at  $294.6$  and  $305.4\text{ cm}^{-1}$ , shoulders on the side of the  $\nu_{12}$  MF monomer at  $318\text{ cm}^{-1}$ . They belong to the 1:1 complex because follow linearly monomers concentration. Three other weaker bands at  $248$ ,  $471$ , and  $482\text{ cm}^{-1}$  are also attributed to the 1:1 complex. As discussed later, all these bands are intermolecular bands. Another band appears at  $352\text{ cm}^{-1}$  near the  $\nu_{17}$  MF mode and belongs to 1:1 complex too, but this one is attributed to the intra  $\nu_{17}$  MF mode perturbed by water.



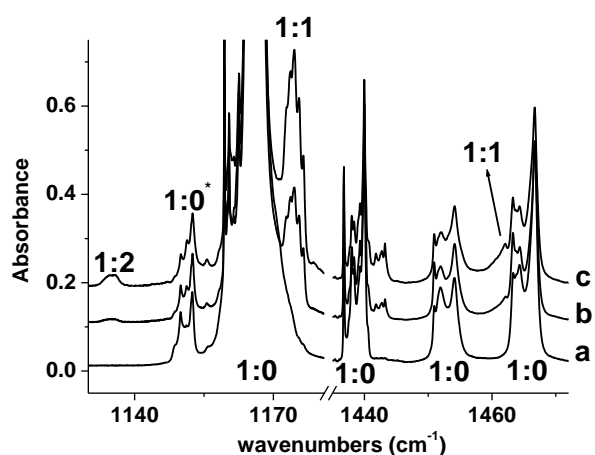
**Fig. 2.** Spectra in the  $80\text{-}500\text{ cm}^{-1}$  region at  $3\text{ K}$  deposition, with different MF/H<sub>2</sub>O/Ne concentration ratios. (a) 0/9/1000, (b) 6/0/1000, (c) 6/3/1000, (d) 6/9/1000.

#### 4.2.2 MF spectral regions

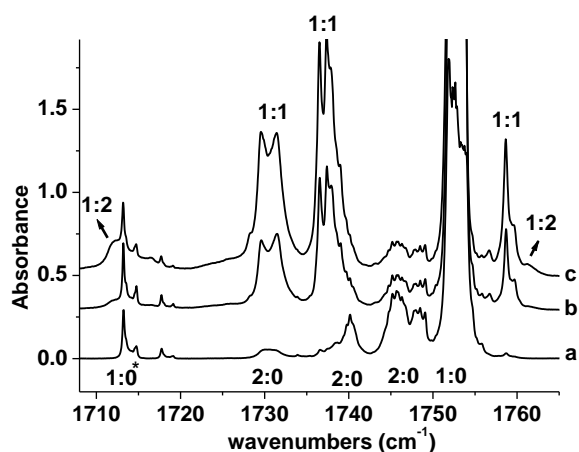
We observe ten fundamental modes of MF perturbed by one or two water molecules. The regions of some MF modes are showed in Fig. 3-6 and signatures attributed to the 1:1 complex appear since they follow the intensity evolution of the MF or H<sub>2</sub>O concentration. The figures of the  $\nu_8$  and  $\nu_7$  regions are reported in the supplementary material (see figures S1 and S2). We also observe, in Fig. 4 and 5, one band at  $1135\text{ cm}^{-1}$  and two bands at  $1712.0$  and  $1761.2\text{ cm}^{-1}$ , respectively, due to the 1:2 complex because following the intensity evolution of the water dimer bands.



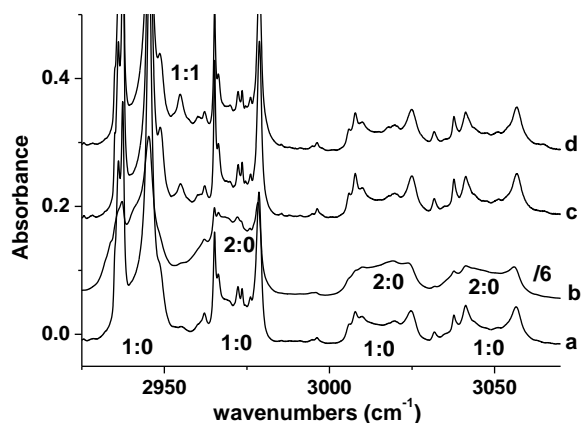
**Fig. 3.** Spectra in the MF  $\nu_{11}$  and  $\nu_{10}$  regions at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 1/0/1000, (b) 1.5/9/1000, (c) 9/9/1000.



**Fig. 4.** Spectra in the MF  $\nu_9$ ,  $\nu_6$ ,  $\nu_{14}$ , and  $\nu_5$  regions at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 1/0/1000, (b) 1/3/1000, (c) 1/6/1000. The asterisk on 1:0 near 1150 cm<sup>-1</sup> indicates the <sup>13</sup>C MF  $\nu_9$  band.



**Fig. 5.** Spectra in the MF CO stretching  $\nu_4$  region at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 10/5/1000, (b) 10/10/1000, (c) 10/0/1000. The asterisk on 1:0 near 1710 cm<sup>-1</sup> indicates the <sup>13</sup>C MF  $\nu_4$  band.



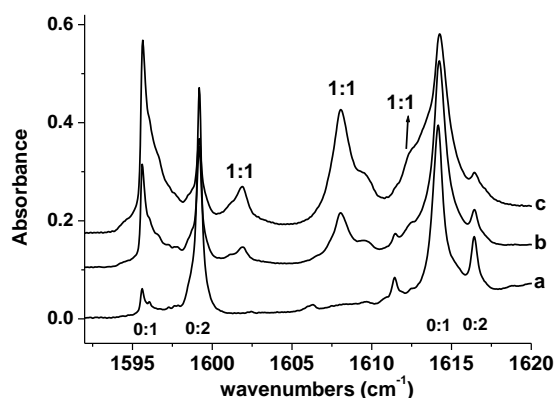
**Fig. 6.** Spectra in the MF  $\nu_3$  regions at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 1.5/0/1000, (b) 9/0/1000 with the absorbance scale divided by 6, (c) 1/3/1000, (d) 1/9/1000 .

#### 4.2.3 H<sub>2</sub>O spectral regions

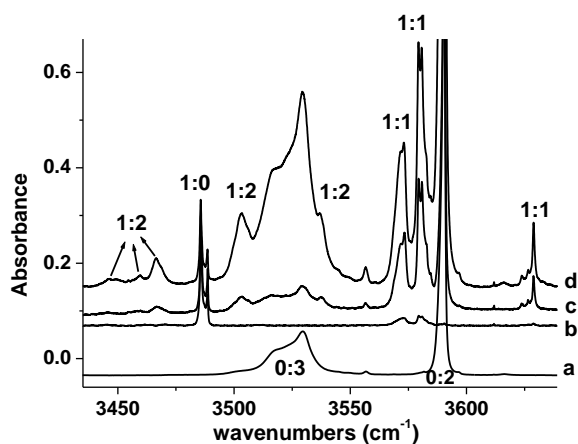
In the H<sub>2</sub>O bending  $\nu_2$  region (Fig. 7) three new bands appear at 1601.9, 1608.1, and 1612.6 cm<sup>-1</sup> when MF is added to H<sub>2</sub>O and are assigned to the 1:1 complex. The last one is a shoulder on the Q(1) monomer band at 1614.2 cm<sup>-1</sup>.

In the H<sub>2</sub>O  $\nu_1$  region (Fig. 8) three groups of signatures, a doublet at 3571.7, 3573.4, a doublet at 3579.4, 3580.8, and a band at 3628.8 cm<sup>-1</sup> follow linearly the concentration of H<sub>2</sub>O or MF and are attributed to 1:1 complex. At higher water concentration several signatures at 3447.5, 3459.6, 3466.9, 3503.1, and 3537.6 cm<sup>-1</sup> grow like the signature of H<sub>2</sub>O dimer and are attributed to 1:2 complex.

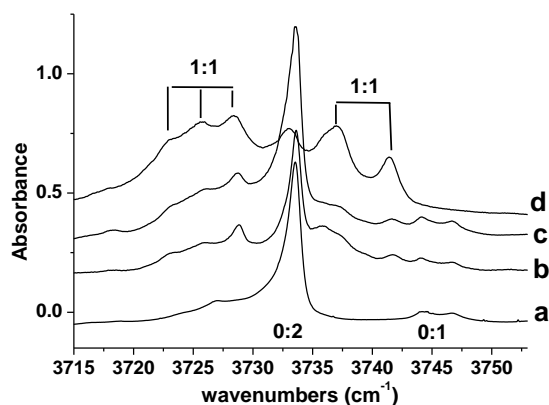
In the H<sub>2</sub>O  $\nu_3$  region (Fig. 9) two groups of bands at 3723.4, 3725.8, 3728.5 cm<sup>-1</sup> and at 3736.9, and 3741.5 cm<sup>-1</sup> appear around the H<sub>2</sub>O dimer signature at 3733.7 cm<sup>-1</sup> and are attributed to the 1:1 complex.



**Fig. 7.** Spectra in the H<sub>2</sub>O  $\nu_2$  region at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 0/1/1000, (b) 1/1/1000, (c) 3/1/1000.



**Fig. 8 .** Spectra in the H<sub>2</sub>O  $\nu_1$  region at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 0/2/1000, (b) 1/0/1000, (c) 1/3/1000, (d) 1/9/1000.



**Fig. 9 .** Spectra in the H<sub>2</sub>O  $\nu_3$  region at 3 K deposition, with different MF<sub>2</sub>/H<sub>2</sub>O/Ne concentration ratios. (a) 10/5/1000, (b) 10/10/1000, (c) 10/0/1000.

#### 4.2.4 Multiquanta transitions

In the  $2\nu_2$  water region two bands attributed to the 1:1 complex are observed at 3176.8 and 3179.3 cm<sup>-1</sup> near the  $2\nu_2$  overtone of the H<sub>2</sub>O dimer. In the near infrared we can attribute, in comparison with the water dimer data, three bands at 5166.9, 5178.5 and 5213.8 cm<sup>-1</sup> and a band at 5124 cm<sup>-1</sup> to the  $\nu_1+\nu_2$  combination for the 1:1 and 1:2 complexes, respectively (Table 3). For the 1:1 complex, we can also attribute two groups of bands at 5319.3 and 5324.9 cm<sup>-1</sup> and at 7219.9 and 7232.1 cm<sup>-1</sup> to the  $\nu_2+\nu_3$  and  $\nu_1+\nu_3$  combinations, respectively. At 1911.4 cm<sup>-1</sup> we observe a 1:1 band which is the combination of the H<sub>2</sub>O  $\nu_2$  bending mode with the intermolecular vibration observed at 305 cm<sup>-1</sup> (see figure S3 in the supplementary material).

## 5. Vibrational assignments and discussion

As we have previously shown in studies of hydrogen bonding complexes [29-31] following the effect of complexation by using the frequency shift between the monomer and complexes ( $\Delta\nu = \nu_{\text{mono}} - \nu_{\text{complex}}$ ) is a good spectroscopic diagnosis to match the observed bands with modes of the different complexes. Also the comparison between observed and calculated data is essential to help the vibrational analysis. It can be noted that some calculated vibrations are not observed for two reasons: many have experimental and/or calculated intensities that are too low and others must be hidden by other monomer or complex absorptions.

### 5.1. MF dimer

We observe 13 modes (Table 1) attributed to the MF dimer. For the most intense band  $\nu_4$ , (the C=O stretching) several signatures are observed and cannot be only different trapping sites, as is the case for  $\nu_{11}$ ,  $\nu_{16}$ , and  $\nu_8$ , because of their annealing compoment and of the large frequency shifts between the bands. The most likely hypothesis is that they are the signatures of different isomers. Actually as mentioned in the theoretical results section three isomers have been calculated with very close binding energy 3.9, 3.9, and 3.8 kcal/mol, so all can be observed in the matrix. We report in the supplementary material all the frequencies and intensities of these isomers in Table S3. It is difficult to associate each observed frequency to a specific isomer because they have very similar calculated frequencies. However, it was possible for  $\nu_4$  mode since we observe four bands with a large frequency shifts between them. We can compare the shifts between monomer and dimers  $\Delta\nu = \nu_{\text{mono}} - \nu_{\text{dimer}}$  of the four observed signatures with the calculated shifts of the four most intense ones (see Tables 1 and S3), two intensities are close zero. We find 3, 7, 12, and 21  $\text{cm}^{-1}$  for the observed ones and 4, 6, 12, and 22  $\text{cm}^{-1}$  for the calculated ones for D1, D2, and D3 isomers for the first three ones and D2 for the last one. The first three values correspond to MF dimer  $\nu_{\text{as}}$  C=O stretching mode and the last to the  $\nu_s$  C=O stretching mode. The agreement between observed and calculated values is very good. This analysis highlights the presence of the three calculated isomers in the matrix.

## 5.2. MF-H<sub>2</sub>O complex

From the concentration effects, attributions have been clearly established for the 1:1 complex. According to the calculations three isomers F1, F2 and F3 can be observable, F1 and F2 have close binding energies (4.6 and 4.1 kcal/mol, respectively), F3 is less stable (2.6 kcal/mol). So to go further in the assignment, thanks to the comparison of the theoretical and experimental values  $\Delta\omega$  or  $\Delta\nu$  we can suggest an attribution of the observed signatures to a specific isomer. In Table 4 we report the calculated harmonic and observed frequencies and intensities and the corresponding shifts for H<sub>2</sub>O and MF modes and for intermolecular modes. All the calculated modes for the three 1:1 isomers are given in the Table S4 of the supplementary material. Also, for almost all the bands attributed to the F1 or F2 isomer, we can observe at least two trapping sites (Tables 2 and 3, Fig.3-5, 8, 9) and these are the average frequencies of the sites which are reported in Table 4. Experimentally the intensities of the bands associated at F3 isomer are less intense compared to those of F1 or F2, while the calculated intensities are often similar between the three isomers. This indicates that F3 is less formed in the matrix due to its lower stability, the calculations don't take account of the probability to form the isomers according to the stability and influence of the matrix cage.

**Table 4**

Comparison of frequencies<sup>a</sup> (cm<sup>-1</sup>) and shifts<sup>a</sup> ( $\Delta\nu = \nu_{\text{mono}} - \nu_{\text{complex}}$ ) between observed and calculated data for the F1, F2, and F3 isomers of the 1:1 complex. The intensities are in parenthesis.<sup>b</sup>

Modes	Calculated						Experimental		Isomer
	F1		F2		F3		$\nu$	$\Delta\nu$	
	$\omega$	$\Delta\omega$	$\omega$	$\Delta\omega$	$\omega$	$\Delta\omega$			
<b>H<sub>2</sub>O</b>									
$\nu_3$	3912(128)	+36	3917 (128)	+31	3922(147)	+26	3725(350) <sup>c</sup>	+36	F1
							3729(260)	+30	F2
							3740(280) <sup>c</sup>	+20	F3
$\nu_1$	3718(277)	+104	3707(277)	+115	3772(118)	+50	3572(560) <sup>c</sup>	+93	F2
							3580(830) <sup>c</sup>	+85	F1
							3629(100)	+37	F3
$\nu_2$	1649(79)	-21	1643(122)	-15	1633(73)	-5	1602(60)	-5	F3
							1608(170)	-12	F2
							1613(150)	-17	F1
<b>MF</b>									
$\nu_3$	3104(14)	-8	3099(21)	-3	3098(23)	-2	2955(50)	-9	F1
$\nu_4$	1757(331)	+12	1750(289)	+19	1774(268)	-5	1731(700) <sup>c</sup>	+21	F2
							1737(1000) <sup>c</sup>	+15	F1
							1759(270)	-7	F3
$\nu_5$	1516(18)	+3	1518(11)	+1	1520(10)	-1	1462(30)	+5	F1
$\nu_6$	1481(9)	-2	1479(5)	0	1479(2)	0	1443(60)	-3	F1
$\nu_7$	1406(2)	-7	1408(2)	-9	1406(6)	-7	1381(3)	-6	F1 or F2 or F3
$\nu_8$	1272(251)	-25	1265(300)	-18	1230(141)	+17	1222(1000) <sup>c</sup>	-11	F2
							1231(700)	-20	F1
$\nu_9$	1202(41)	-9	1200(49)	-7	1181(176)	+12	1175(600)	-8	F1 or F2
$\nu_{10}$	943(28)	+11	955(27)	-1	949(43)	+5	916(170) <sup>c</sup>	+12	F1
$\nu_{11}$	775(5)	-3	778(7)	-6	768(11)	+4	765(3)	+4	F3
							771(30)	-6	F2
							775(20)	-2	F1
$\nu_{17}$	352 (12)	-5	357(19)	-10	344(35)	+3	352(130)	-12	F2
<b>Inter<sup>d</sup></b>									
	539(72)		517(71)		443(111)		482(120)		F2
							471(200)		F1
	348(127)		374(130)		274(102)		305(600)		F2
							295(440)		F1
							248(80)		F3
	139(119)		65(113)		84(75)		110(70)		F1
	97(9)		61(15)		40(14)		104(90)		F1

<sup>a</sup>Rounded calculated and experimental values.

<sup>b</sup>Intensity in km/mol for calculated ones and normalized on the most intense MF  $\nu_4$  mode ( $I_{\nu_4} = 1000$ ) for experimental ones.

<sup>c</sup>Mean frequency of a doublet or multiplet assigned to 1:1 complex trapped in different matrix sites (see Table 1).

<sup>d</sup>Intermolecular modes.

We observe the three water modes perturbed by the complexation and for each one we observe three signatures that we can attribute, with the help of calculations, to the isomers F1, F2 and F3 (Table 4). The



agreement between observed and calculated  $\Delta\nu$  is very good. For the MF modes perturbed by the presence of water, we can also associate for each signature an isomer except for  $\nu_7$  and  $\nu_9$  for which the calculated frequencies are too close to distinguish between isomers. We can notice that for the O-C-O bending  $\nu_{11}$  and for the intense C=O stretching  $\nu_4$  modes, we observe the signatures of the three isomers (Table 4), and for the C-O stretching  $\nu_8$  mode, we observe the signatures of two isomers.

We observe in the far infrared, domain of the intermolecular modes, different bands that can also be attributed to the isomers of the 1:1 complex, reported at the bottom of Table 4. Two signatures at 482 and 471  $\text{cm}^{-1}$ , the last one being twice as intense, are very close and can be attributed to F2 and F1, respectively. The comparison between experimental and calculated frequencies allows us to exclude the F3 isomer. We attribute the bands at 305, 295, and 248  $\text{cm}^{-1}$  to F2, F1, and F3 respectively. The vibrations at 110 and 104  $\text{cm}^{-1}$  are the signature of F1. The band at 352  $\text{cm}^{-1}$  is assigned to the  $\nu_{17}$  MF mode and not to an intermolecular band since this is impossible if we take into account the calculated  $\Delta\nu$ .

We show with the help of calculations the evidence of the presence of 3 isomers of the 1:1 complex in the neon matrix. For some multiquanta transitions, we can specify assignments. For to the  $\nu_2+305$  combination, at 1911.4  $\text{cm}^{-1}$ , an anharmonicity coefficient  $X_{ij}$  of -2  $\text{cm}^{-1}$  can be deduce and this small value for an intra- and an intermolecular mode combination has already been reported for other hydrogen bonding complex [29,30]. For to the  $\nu_1+\nu_2$  combinations, the bands at 5166.9 and 5178.5  $\text{cm}^{-1}$  are the combinations of 3572+1608  $\text{cm}^{-1}$  and 3580+1613  $\text{cm}^{-1}$  for the F1 and F2 isomers, respectively (see Table 4). The deduced  $X_{ij}$  coefficients, -14 and -13  $\text{cm}^{-1}$ , are very near the PD dimer value of -16  $\text{cm}^{-1}$  [27] since in the 1:1 complex the water molecule is the proton donor as a water molecule in the water dimer. The band at 5213.8  $\text{cm}^{-1}$  is the  $\nu_1+\nu_2$  combination for the F3 isomer since this one has the higher  $\nu_1$  and  $\nu_2$  frequencies values, and a  $X_{ij}$  coefficient of -17  $\text{cm}^{-1}$  can be deduce. For the  $\nu_2+\nu_3$  combinations, the bands at 5319.3 and 5324.9  $\text{cm}^{-1}$  can probably be assigning to the F1 and F2 isomers, and for the  $\nu_1+\nu_3$  combinations, the positions of the  $\nu_1$  bands imply the assignment of the bands at 7219.9 and 7232.1  $\text{cm}^{-1}$  to the F2 and F1 isomers, respectively. The deduced  $X_{ij}$  coefficients, -81 and -73  $\text{cm}^{-1}$ , are very near the PD dimer value of -87  $\text{cm}^{-1}$  [27].

## 5.2. MF-(H<sub>2</sub>O)<sub>2</sub> complex

According to the calculations three isomers G1, G2, and G3 (Fig. 1) can be observable since they have relatively close binding energies (8.6, 7.8, and 6.9 kcal/mol, respectively). When the concentration of water is important we observe bands attributed to the 1:2 complex: five signatures for the  $\nu_1$  H<sub>2</sub>O mode and one and two ones for  $\nu_9$  and  $\nu_4$  MF modes, respectively. In Table 5 we compare the experimental and calculated shifts of the three isomers. The water vibrations are compared with those of the water dimer and the MF ones with those of the MF monomer.

We see that it is difficult to distinguish the G2 or G3 signatures because their calculated frequencies for the H<sub>2</sub>O modes are very close (see the Table S5 of the supplementary material). However we attribute three frequencies to the  $\nu_1$  PD and three ones to the  $\nu_1$  PA of H<sub>2</sub>O dimer perturbed by the MF molecule. Two bands are clearly the signature of G1 but we cannot conclude definitively for the others  $\nu_1$  PD and PA bands (Table 5). For MF modes we conclude without ambiguity in view of the shift that the  $\nu_9$  observed band is the signature of G3 and the two  $\nu_4$  ones those of G2 and G1. We can notice again that we observe a very good match between experimental and calculated values. So we can conclude that we observe the presence of the three isomers G1, G2, and G3 of 1:2 complex in the neon matrix.

**Table 5**

Comparison of frequencies<sup>a</sup> (cm<sup>-1</sup>) and shifts ( $\Delta\nu = \nu_{\text{mono}} - \nu_{\text{complex}}$ )<sup>b</sup> between observed and calculated data for the G1, G2, and G3 isomers of the 1:2 complex. The intensities are in parenthesis.<sup>c</sup>

modes	Calculated						Experimental		Isomer
	G1		G2		G3		$\nu$	$\Delta\nu$	
	$\omega$	$\Delta\omega$	$\omega$	$\Delta\omega$	$\omega$	$\Delta\omega$			
H <sub>2</sub> O									
$\nu_1$ PD	3639 (310)	+80	3576 (430)	+143	3580 (465)	+139	3448(26) 3460(17) 3503(1000)	+143 +131 +87	G2 or G3 G2 or G3 G1
$\nu_1$ PA	3694 (412)	+120	3627 (789)	+187	3620 (368)	+194	3460(17) 3467(440) 3538(250)	+201 +194 +123	G2 or G3 G2 or G3 G1
MF									
$\nu_9$	1162 (259)	+29	1199 (55)	-6	1200 (96)	-7	1135(110)	+32	G1
$\nu_4$	1770 (183)	-1	1729 (324)	+40	1691 (278)	+78	1712(140) 1761(400)	+40 -9	G2 G1

<sup>a</sup>Rounded calculated and experimental values.

<sup>b</sup>The shifts for the water vibrations in the complex are compared with those of the water dimer

<sup>c</sup>Intensity in km/mol for calculated ones and normalized on the most intense  $\nu_1$ PD ( $I= 1000$ ) for experimental ones.

### 5.3. Comparisons with other MF-water systems

Some works studied the interaction between MF molecule and water ices because of the interest in interstellar chemistry [22,23]. At 20 K, a MF-water mixed ice work shows infrared spectra with a broad C=O band located at  $1716\text{ cm}^{-1}$  [23], red-shifted by  $38\text{ cm}^{-1}$  in comparison with the gas phase value [8-10]. In solid neon for 1:2 complex we observe a C=O band at  $1712\text{ cm}^{-1}$ , red-shifted by  $41\text{ cm}^{-1}$ , frequency shift very similar to the one observed in the MF-water mixed ice. This observation suggests that the interaction between the MF molecule and two water molecules is sufficient to start assessing the influence of a mixed ice effect.

The complex of dimethyl carbonate ( $\text{CH}_3\text{O}(\text{C}=\text{O})\text{OCH}_3$ ) with water was studied by infrared in solid nitrogen and by calculations at the B3LYP level [32]. A 1:1 complex was identified where the carbonyl oxygen served as the proton acceptor and the water's oxygen is directed to the  $\text{CH}_3$  group like our F1 1:1 MF-water complex (Fig. 1). The observed C=O shift,  $16\text{ cm}^{-1}$ , is very similar to ours ( $15\text{ cm}^{-1}$ ) for the F1 isomer. Another complex was calculated whereas the alkoxy oxygen was the proton acceptor, like our F3 1:1 MF-water complex, but the authors don't observe it.

## 6. Conclusion

For the first time an experimental vibrational analysis of the MF dimer and the MF-H<sub>2</sub>O and MF-(H<sub>2</sub>O)<sub>2</sub> complexes has been carried out in solid neon from the near to the far infrared. On the basis of concentration effects we assign the observed bands to the 2:0, 1:1, and 1:2 complexes. With the help of calculations we are able to prove for these three complexes that different isomers are formed in the matrix and we can distinguish between them. We highlight the presence of three isomers for the MF dimer especially by the observation of three different signatures for the C=O stretching mode  $\nu_4$ . For the 1:1 complex we observe 31 signatures that are almost all associated with one of the three calculated isomers. Careful examination of the far infrared region allows the assignment of several 1:1 intermolecular modes. By

observing the  $\nu_1$  PD and PA of H<sub>2</sub>O dimer perturbed by the MF molecule and with the observation of two intense MF modes we conclude that three isomers of the 1:2 complex are present in the Ne matrix.

This study of weak hydrogen-bonded complexes shows again the importance of the neon matrix isolation technique in combination with the Fourier Transform infrared spectroscopy in order to obtain a wide range of vibrational data from the intermolecular mode to the combinations and overtones domains. The analysis of these data allows us to highlight the existence of different isomers thanks to the contribution of ab initio calculations, showing the importance of the complementarity between theory and experience.

### **Declaration of competing interest**

The authors declare that they have no conflict of interest.

### **CRedit authorship contribution statement**

**Pascale Soulard** carried out the experiments, contributed to the data analysis, performed the ab initio calculations, and drafted the manuscript;

**Benoit Tremblay** carried out the experiments, performed the IR analysis and contributed to the manuscript drafting.

### **Supplementary material**

See the supplementary material for calculated Binding energies, Harmonic frequencies, Intensities for the monomers, dimers, and the most stable isomers of 1:1 and 1:2, and figures showing the MF bending  $\nu_8$ ,  $\nu_7$  and the combination of H<sub>2</sub>O  $\nu_2 + \nu_{\text{inter}}$  (305cm<sup>-1</sup>) regions of 1:1 complex.

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